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Electrostatically Self-Assembled Nanocomposite Reactive Microspheres

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ABSTRACT Nanocomposite reactive microspheres with diameters of $\sim 1\text{--}5\ \mu\text{m}$ were created via electrostatic self-assembly of aluminum and cupric oxide nanoparticles. The ability to utilize this novel approach of bottom-up assembly to create these reactive materials allows for the potential for a more intimate mixture between the two nanoreactants and, thus, an overall more energetic combustion process. Experiments with the self-assembled material demonstrate the ability to achieve ignition and sustain a combustion wave in rectangular microchannels, which does not occur with material having similar amounts of organics mixed via the traditional sonication method.

KEYWORDS: electrostatic self-assembly • nanoenergetics • thermites • microspheres

The ability to create crystalline aggregates of a binary system of nanoparticles (NPs) from the bottom up has been of great interest to various scientific fields such as catalysis (1), solar cells (2), biological tags (3), optoelectronics (4), and magnetic recording media (5). Recently, electrostatic forces have been utilized to assemble the two constituents, as opposed to attractive van der Waals or entropic forces, allowing for a wide array of non-close-packed structures to be created without relying on particle size differences. Research on electrostatic nanoparticle self-assembly has focused mainly on understanding the fundamental physics that govern the phenomenon and characterization of the final structures, rather than direct applications (6–10). This work directly applies this bottom-up assembly approach to the field of energetic materials, in particular nanoscale thermites, to create electrostatically self-assembled nanocomposite reactive microspheres with diameters from 1 to $5\ \mu\text{m}$ (Figure 1). Furthermore, combustion experiments are performed with these novel materials to assess their reactive properties and applicability.

Nanoscale thermites are a relatively new reactive material that consist of a metallic fuel and a metal oxide oxidizer, both in the form of a powder with particles having critical dimensions on the nanoscale (11). The standard mixing procedure (no electrostatic self-assembly used) calls for a solution of the two constituents in hexanes ($\sim 70\ \text{g/L}$), mixed via sonication at an appropriate equivalence ratio (ϕ). Aluminum NPs, nAl (purchased from Novacentrix Inc.), and cupric oxide NPs, nCuO (purchased from Sigma-Aldrich), with average diameters of ~ 38 and $\sim 33\ \text{nm}$, respectively

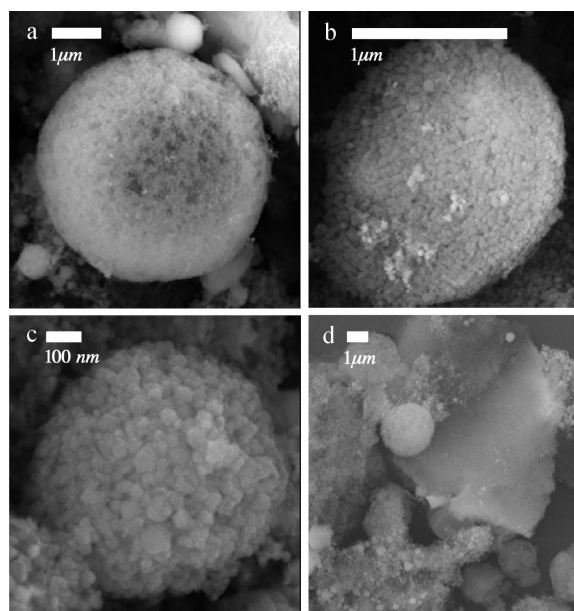


FIGURE 1. Scanning electron micrographs of self-assembled nanocomposite reactive microspheres composed of aluminum and cupric oxide nanoparticles. Images a–c show details of various microspheres. Image d is an example of the modest yield of microspheres created by the self-assembly process.

(company specification), are the constituents used in this work, which have been shown to have an optimum equivalence ratio of 1.1 with regards to combustion properties (12). The solution is sonicated with a 200 W sonic horn for 1 min at a 50 % duty cycle and subsequently placed on a hot plate ($\sim 40\ ^\circ\text{C}$) to dry. Recently, sonicated thermites have been shown to propagate a reaction in rectangular microchannels having hydraulic diameters from ~ 100 to $800\ \mu\text{m}$ (the image is given in the Supporting Information) (13). These microchannels will be used for the combustion experiments in this work. Flame velocities are typically steady and range from approximately 100 to 700 m/s, depending on a variety of parameters, including the oxidizer and diluent species,

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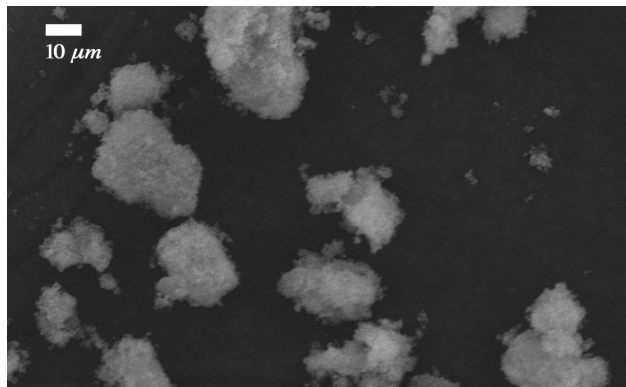


FIGURE 2. Scanning electron micrograph of amorphous aggregates of nAl and nCuO created using the sonication method to mix the nanoscale thermite.

diluent concentration, stoichiometry, particle size, and channel dimensions.

Sonication is an efficient and straightforward method of mixing the nanoparticle constituents; however, there are drawbacks and limitations. This top-down approach creates amorphous aggregates that are highly unorganized and nonuniform (Figure 2). Even though the constituents have dimensions on the nanoscale, the overall diffusion and mixing length scales associated with the reactivity are larger due to the aggregation of like species. Furthermore, sonication is not a viable method for mixing if the production of these materials is to be scaled up for practical use.

Ideally, a repeatable method of bottom-up assembly would be utilized to have each fuel particle surrounded by only oxidizer particles and vice versa, forming a binary nanoparticle lattice structure (6, 7, 9). The diffusion and mixing length scales would then be limited by only the particle dimensions, allowing for the full energetic potential to be realized. This work presents the first steps toward building nanoenergetic materials from the bottom up using electrostatic self-assembly and validating their applicability with combustion experiments.

The surface of the nAl is coated with an ω -functionalized alkanolic acid, $\text{COOH}(\text{CH}_2)_{10}\text{NMe}_3^+\text{Cl}^-$, or TMA (purchased from Prochimia Inc.) and the surface of the nCuO with an ω -functionalized alkanethiol (14), $\text{SH}(\text{CH}_2)_{10}\text{COO}^-\text{NMe}_4^+$, or MUA (originally purchased from Prochimia Inc. as $\text{SH}(\text{CH}_2)_{10}\text{COOH}$; the treatment is described in the Supporting Information). The acid is chosen for the Al and the thiol for the CuO on the basis of past studies of self-assembled monolayers (SAMs) on metal oxide surfaces (15–18) (nAl has an Al_2O_3 passivation shell). When they are in separate solutions of dimethyl sulfoxide (DMSO) (10 mM), the functionalized particles remain suspended and unaggregated for several weeks. As the nAl solution is added to the nCuO solution, the charge is neutralized and the two constituents self-assemble and precipitate out of solution over several hours. Upon assembly, ammonium salts are formed which may hinder full crystallization. The salts are washed with acetonitrile, the precipitate is redissolved in a 1/4 v/v mixture of acetonitrile and DMSO, and the temperature is increased

to 80 °C. A modest yield of well-defined microspheres is grown overnight by slow evaporation of the acetonitrile (Figure 1).

To create a higher yield of well-defined microspheres, the elevated temperature, low concentration overnight growth step is necessary. However, due to the low concentration of energetic material used, this step allows for only microgram quantities to be prepared in the laboratory, which is insufficient for combustion experiments. Therefore, for synthesis of material to be used in combustion experiments, the slow-growth step is not utilized. Examination of scanning electron microscopy (SEM) images of the self-assembled material at this point in the synthesis shows microspheres that contain more flaws and inclusions (see the Supporting Information). Sufficient quantities (~50 mg) of material, however, can be synthesized and tested. Moreover, the precipitation of the two constituents out of solution upon mixing strongly suggests electrostatic self-assembly has occurred and is the sole source of mixing used.

Another aspect of the assembly that must be taken into account for the combustion experiments is the overall stoichiometry of the system. The molar ratio of Al to CuO must be at 1:1.36, to give $\phi = 1.1$ (12), which is the predetermined optimum stoichiometry for combustion. Depending on particle sizes used and oxide layer thickness on the nAl, this ratio may not coincide with the optimum ratio for full assembly of the two constituents and some material may remain in solution. However, for the particles used in this work, the optimum equivalence ratio was forced and the supernatant appeared clear after self-assembly. Therefore, full precipitation is assumed to have occurred and the mixture is at the optimum equivalence ratio.

To fully understand the effect of utilizing electrostatic self-assembly as a means of mixing energetic materials, combustion characteristics in microchannels are examined. The microchannels are loaded with ~2 mg of material, and a spark ignition source is placed at one end. The filled microchannel is placed in an explosion-proof chamber with viewing windows. A high-speed camera is utilized to capture images of the combustion wave and measure propagation rates.

As a baseline experiment, nAl and nCuO are mixed via sonication as per the method mentioned previously with no ligands present in the matrix. The materials are mixed at the optimum equivalence ratio of 1.1, which corresponds to mass percentages of 33.7% nAl and 66.3% nCuO. This accounts for the Al_2O_3 passivation shell on the nAl, which was shown via thermogravimetric analysis (TGA) to be about 51% of the mass of the nAl particle (Supporting Information). Three experiments were performed, and an average propagation rate of 285 ± 17 m/s was demonstrated.

For a full understanding of the effects of mixing via electrostatic self-assembly, the hydrocarbon ligands present in the self-assembled material must be taken into account when examining the reactive properties. To clearly compare the effects of mixing via self-assembly to mixing via sonication, an experiment is performed whereby the sonicated

nAl and nCuO are initially coated with nonfunctionalized hydrocarbon ligands of length similar to that of the ligands used for self-assembly (1-dodecanoic acid on nAl and 1-dodecanethiol on nCuO). These ligands are termed as “blank ligands”. This allows for similar amounts of hydrocarbon material within the energetic matrix and alleviates the effects of their mere presence on combustion characteristics, allowing for a clear understanding of how the reactive properties are influenced by self-assembly alone.

When the blank ligands are used to coat the nAl and nCuO, they account for 3% and 11% of the total mass, respectively, as per TGA results (Supporting Information). Taking the hydrocarbon coatings into account, a mixture with an equivalence ratio of 1.1 will have 31.8% coated nAl and 68.2% coated nCuO by mass. This mixture was sonicated in hexanes, dried, and loaded into the microchannel exactly as for the preparation of the baseline material. A relatively small amount of sonicated, bare (no hydrocarbon ligands added) nAl/nCuO thermite is placed at the spark to act as a primer. Three experiments were run, and for each, the primer was ignited and the camera was subsequently triggered. This material, however, was unable to ignite and sustain a combustion wave. This brings about significant concern that the hydrocarbon ligands diluted the material beyond its combustion limits.

To further understand the effects of the hydrocarbon ligands on the combustion of the nAl/nCuO nanoscale thermite, constant-volume equilibrium calculations were performed (CHEETAH 4.0 (19) with the JCZS product library (20)) and the equilibrium temperature was examined. The initial mixture consisted of 1-dodecanoic acid, 1-dodecanethiol, aluminum, aluminum oxide, copper oxide, and air with the proper mass percentages and overall density reflecting the experiments. The equilibrium temperature for the thermite without hydrocarbon ligands (Al_2O_3 passivation shell included) is 3149 K. If the hydrocarbon ligands are included in the calculation, the equilibrium temperature drops by 18% to 2592 K. This demonstrates the significant dilution effect brought about by the addition of the hydrocarbon ligands within the thermite matrix.

The fact that the ligands are present within the self-assembled material could be detrimental to their ability to ignite and self-sustain a reaction. If, however, the self-assembly process brings about more intimate mixing, which is a primary goal for this work, the self-sustaining combustion process may still have a chance to present itself. Due to the limited quantities of self-assembled material, the weight percent of the functionalized ligands was not examined via TGA and is assumed to be the same as what is found for the blank ligands. The fact that these materials are bound to the surface in the same manner and the molecular weights of the functionalized ligands are higher than those of the blank ligands makes this a conservative assumption.

The self-assembled material is loaded into the microchannel and primed similar to the thermite coated with blank ligands. Unlike the material with the blank ligands, the self-assembled material is able to successfully achieve igni-

tion and propagation of the reaction. This strongly suggests that the self-assembly process allows for a more intimately mixed material that will lead to more desirable combustion properties.

The propagation is bimodal in nature (images of the reaction along with the trajectory plot shown in the Supporting Information demonstrate the bimodal nature of the propagation). The first mode propagates to about one-fourth of the length of the channel at approximately 10 m/s, while the second mode travels at about 0.25 m/s for the remainder of the length. It is noted that there is a significant decrease in performance from the baseline material (sonicated, bare nanoscale thermite); however, it was able to ignite and self-sustain a propagation, unlike the sonicated material with similar amounts of hydrocarbons within the matrix. This comparison is more meaningful, due to the fact that the diluent content is taken into account.

The use of self-assembly to mix nanoscale thermites could create a new avenue for building energetic nanocomposites from the bottom up. This could potentially lead to custom tailoring of the reactive properties based on the nanoscale structure and allow for a more complete understanding of the physics governing the propagation. More accurate combustion models could be created on the basis of the known distribution of species rather than the random nature associated with most heterogeneous energetic materials. Various particle sizes, chain lengths, and atomic species could potentially be varied to incrementally vary the propagation rate and tailor it to the device of interest.

This work is the first to implement self-assembly to create nanocomposite reactive microspheres, and experiments were applied to analyze their reactive properties. The microspheres had diameters approximately 2 orders of magnitude greater than those of the constituent nanoparticles, demonstrating a bottom-up assembly process. Unlike sonicated material with similar amounts of hydrocarbon ligands, these materials show the ability to ignite and self-sustain a reaction in channels with dimensions on the microscale. This empirically suggests that a more ordered structure favorable for reaction is created by the self-assembly process.

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Supporting Information Available: Text (part A) providing a detailed method for particle preparation and the self-assembly procedure, Figure S1, showing images of self-assembled microspheres without the elevated temperature, low concentration overnight growth step (this material was used in the combustion experiments due to the higher yield of material synthesized), text (part B) describing the TGA conditions used for analysis of coated and uncoated aluminum and copper-oxide nanoparticles, with an equation (eq S1) that was used to calculate the percent mass of active aluminum present in the nAl powder, Figure S2, giving the results of the TGA experiments, Figure S3, giving images of the microchannel flame propagation for both the baseline

and self-assembled material along with a trajectory plot of the self-assembled material, Figure S4, giving an image of the microchannel used for combustion experiments, and Figure S5, giving a schematic of aluminum and cupric oxide nanoparticles with their respective ligands used for self-assembly. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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